

# PATENT ABSTRACTS OF JAPAN

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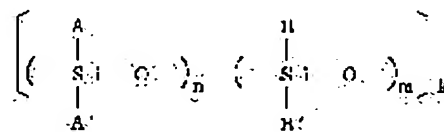
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## (54) LITHIUM NONAQUEOUS SECONDARY BATTERY

(57)Abstract:

**PURPOSE:** To obtain a high-performance lithium nonaqueous secondary battery with its excellent cycle characteristics capable of charging even at a high current density by containing a silicone compound is an electrolytic liquid or solid electrolyte.

**CONSTITUTION:** A compound shown by expression I is contained in electrolytic liquid or solid electrolyte in a nonaqueous secondary lithium battery in which a host compound forming a lithium metal, a lithium alloy, or a lithium ion and an interlayer compound, or complex is formed in a negative pole. In this expression, n stays in a range from 0 to 10, and m and k stay in a range from 1 to 10. A and A' express alkyl groups which may be the



same or different from each other, B and B' express an oxyalkylene chain or alkyl group which does not have an active hydrogen which may be the same or different from each other, however, at least one of B and B' is an oxyalkylene chain which does not have any active hydrogen.

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## CLAIMS

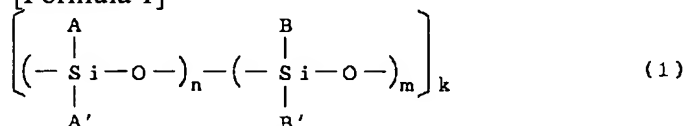
[Claim(s)]

[Claim 1] The lithium cell characterized by containing a silicone system compound in the electrolytic solution or a solid electrolyte in the nonaqueous rechargeable battery which has the negative electrode and electrolyte containing at least one sort of things chosen from the group which consists of a host compound which forms a positive electrode, a lithium metal, a lithium alloy and a lithium, an intercalation compound, or a complex.

[Claim 2] The lithium cell which is the thing of the structure which the oxy-alkylene chain added [ the silicone system compound ] to the side chain of a Si-O frame in the lithium cell according to claim 1.

[Claim 3] It sets to a lithium cell according to claim 1 or 2, and a silicone system compound is a degree type (1).

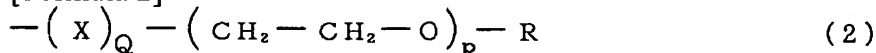
[Formula 1]



(0-10, and m and k of n are 1-10 among a formula.) Same or alkyl group [ which may be different from each other ], B, and B' of A and A' is the same or an oxy-alkylene chain with which at least one side of B and B' does not have active hydrogen although the oxy-alkylene chain or alkyl group which does not have active hydrogen which may be different from each other is expressed. Lithium cell which is what is expressed.

[Claim 4] For the silicone system compound expressed with a front type (1) in a lithium cell according to claim 3, the oxy-alkylene chain of B and B' is a degree type (2).

[Formula 2]



It is the silicone system compound expressed with (1-5p of Q are 1-10 among a formula, R expresses the alkyl group of carbon numbers 1-12, and X expresses the alkylene group or oxy-alkylene chain of carbon numbers 1-6).

[Claim 5] The lithium cell whose main constituent of a host compound is a carbon body in a lithium cell according to claim 1, 2, 3, or 4.

[Claim 6] The lithium cell whose main constituents of a positive electrode are a conductive polymer and/or a transition-metals compound in a lithium cell according to claim 1, 2, 3, 4, or 5.

[Translation done.]

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the nonaqueous secondary lithium cell which uses as a negative electrode the host compound which forms a lithium metal, a lithium alloy or a lithium ion, an intercalation compound, or a complex.

**[0002]**

**[Description of the Prior Art]** The theoretical energy density of a lithium secondary battery is high, and the power source for portable electronic equipment is expected from utilization also as an electric vehicle and a power source for stationary energy storage at first. However, second lithium \*\* which used the metal lithium for the negative electrode has a problem in points, such as a cycle life and safety, and the thing of sufficient engine performance is not developed. It is thought that one of the biggest reason of this is in the engine performance of a negative electrode. Since the reactivity of the metal lithium which is a negative electrode is high as a practical trouble of the negative electrode of a lithium secondary battery, a negative-electrode front face tends to react with a solvent. The metal lithium generated by reduction of a lithium ion at the time of charge is the problem of considering as a dendrite, being easy to generate and destroying the insulating layer between forward and a negative electrode (separator). The additive of the electrolytic solution is examined as one of the approaches of solving these problems [Morita, Aoki, Matsuda, electrification 57,523(1989);M.Morita, S.Aoki and Y.Matsuda, Progress in Batteries & Solar Cells, Vol.8 (1989)]. Development of the negative electrode which used the carbon material which incorporates a lithium ion between its layers into a negative-electrode ingredient, and is stabilized as an intercalation compound or a lithium metal into it on the other hand, and the ceramic ingredient is furthered. The carbon body obtained by calcinating the pyrolytic carbon which used the organic compound besides a natural graphite, coal, and corks as the raw material as INTAKARANTO of a lithium ion, naturally-occurring polymers, and synthetic macromolecule is raised. The gestalt of a carbon fiber and glass-like carbon is also various from porosity fine particles. Using for JP,2-66856,A the conductive carbon material which calcinated furfuryl resin at 1100 degrees C, for example as a negative-electrode active material as a carbon material for these negative-electrodes active materials is proposed. Moreover, the example which uses the conductive carbon material which heat-treats aromatic polyimide at the temperature of 2000 degrees C or more under an inert atmosphere, and is obtained for a negative-electrode active material is indicated by JP,61-277165,A, and using for a negative electrode what graphitized easy-graphite spheroidal carbon is further proposed by JP,4-115457,A at it. Moreover, in JP,61-77275,A, the rechargeable battery which used for the electrode the carbon material of the insulation of the poly acene structure which heat-treated the phenol system macromolecule, or semi-conductor nature is indicated. Although a cycle life improves and the cell engine performance improves in these ion fuel cell subsystems, in one side, it cannot be said that a current characteristic is enough.

**[0003]**

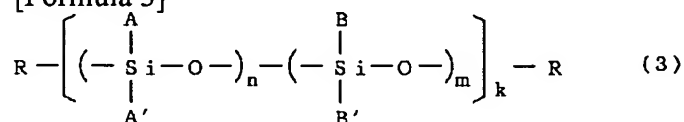
**[Objects of the Invention]** The purpose of this invention solves the current characteristic in these lithium

nonaqueous rechargeable batteries, is excellent in a cycle property, and is to offer the high performance secondary lithium cell in which charge and discharge are possible also with high current density.

[0004]

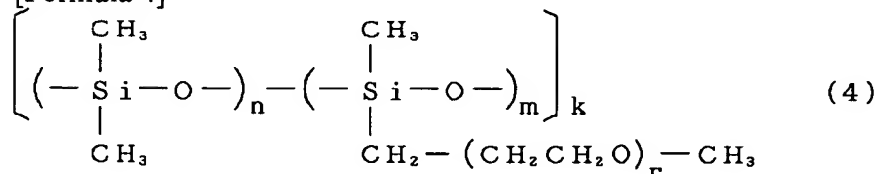
[Elements of the Invention] this invention persons found out that the purpose was reached in the nonaqueous secondary lithium cell which uses as a negative electrode the host compound which forms a lithium metal, a lithium alloy or a lithium ion, an intercalation compound, or a complex by making a silicone system compound contain in the electrolytic solution or a solid electrolyte, as a result of examining said technical problem wholeheartedly. As said silicone system compound, the compound shown by the front formula (1) is mentioned. Remarkable effectiveness was seen in the silicone system compound with which oxy-alkylene adds to the side chain of a Si-O frame, and existence of active hydrogen is not checked especially. If the compound shown by the front formula (1) is shown more concretely, the silicone system compound shown by the degree type (3) will be mentioned.

[Formula 3]



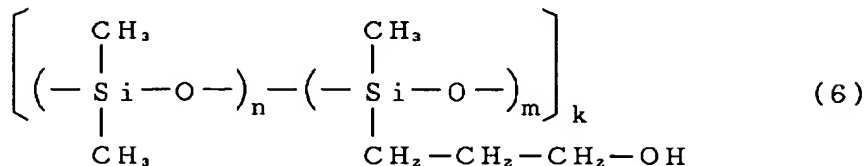
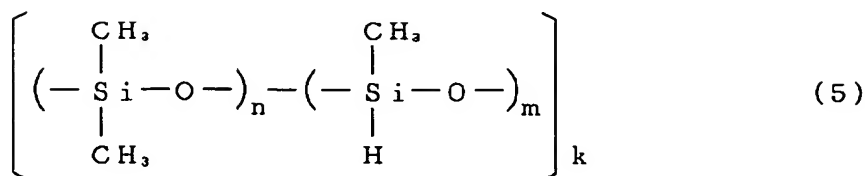
in a front type, R is an end group and this end group is the same -- or -- being different from each other -- desirable -- an alkyl group -- it is a methyl group still more preferably. A and A' is the same or the alkyl group of carbon numbers 1-30 which may be different from each other, and is the alkyl group of carbon numbers 1-6 preferably [ it is desirable and ] to the alkyl group of carbon numbers 1-12, and a pan. B and B' is an oxy-alkylene chain which does not have an alkyl group or active hydrogen and with which at least one side does not have active hydrogen among B and B', although the same, the oxy-alkylene chain which may be different from each other, or an alkyl group is expressed. In addition, when said B and B' are oxy-alkylene chains, it is the oxy-alkylene chain of carbon numbers 1-6 preferably [ it is desirable and ] to the oxy-alkylene chain of carbon numbers 1-12, and a pan. Moreover, when B and B' is an alkyl group, it is the alkyl group of carbon numbers 1-6 preferably [ it is desirable and ] to the alkyl group of carbon numbers 1-12, and a pan. The silicone system compound which has the frame shown especially by the bottom formula (4) made the current characteristic improve, and found out that it was effective for high-energy-izing of a cell.

[Formula 4]



Since a silicone frame generally has a ready bubble operation, a silicone compound is used as a defoaming agent, but in this invention, since nonaqueous electrolyte and compatibility were made to improve and the surface energy of the electrode interface of a nonaqueous cell fell as this result by making an alkoxy group add to a silicone compound, it thinks. Although a front-type (4) compound is obtained by adding CH<sub>2</sub>=CH-CH<sub>2</sub>-OH according to a platinum catalyst, considering as a bottom-type (6) compound, and permuting the active hydrogen of this compound by the bottom-type (5) compound with an oxy-alkylene chain further, as a front-type (4) compound, active hydrogen is measured by IR and that in which active hydrogen does not exist is suitable.

[Formula 5]



In addition, in a front type (4), (5), and (6), 0-10, and m, r and k of n are 1-10. a front type (1) or the compound of (3) -- the solid electrolyte or electrolytic-solution 100 weight section -- receiving -- 0.1 - 30 weight section -- desirable -- 0.1 - 10 weight \*\*\*\*\*.

[0005] Next, although the configuration of the nonaqueous secondary lithium cell of this invention is described concretely, fundamentally, it is constituted by a positive electrode, a negative electrode, and the electrolyte. What dissolved the electrolyte salt in the non-aqueous solvent as the electrolytic solution is mentioned. as a non-aqueous solvent -- a carbonate solvent (propylene carbonate and ethylene carbonate --) Butylene carbonate, dimethyl carbonate, diethyl carbonate, an amide solvent (N-methyl formamide, N-ethyl formamide, and N.N-dimethylformamide --) N-methyl acetamide, N-ethyl acetamide, N-methyl PIROJIRINON, a lactone solvent (gamma-butyl lactone, gamma-valerolactone, and delta-valerolactone --) alcoholic solvents (ethylene glycol --), such as the 3-methyl -1 and 3-oxazolidine-2-ON Propylene glycol, a glycerol, methyl cellosolve, 1, 2-butanediol, 1,3-butanediol, 1,4-butanediol, diglycerol, Polyoxy alkylene glycol, cyclohexane diol, a xylene glycol, etc., an ether solvent (a methylal, 1, 2-dimethoxyethane, 1, and 2-diethoxy ethane --) 1-ethoxy-2-methoxyethane, the alkoxy polyalkylene ether, etc., A nitril solvent (a benzonitrile, an acetonitrile, 3-methoxy propionitrile, etc.), phosphoric acid and a phosphoric ester solvent (orthophosphoric acid, metaphosphoric acid, pyrophosphoric acid, and polyphosphoric acid --) 2-imidazolidinone solvents, such as phosphorous acid and trimethyl phosphate (1,3-dimethyl-2-imidazolidinone etc.), A pyrrolidones solvent, a sulfolane solvent (a sulfolane, tetramethylen sulfolane), A furan solvent (a tetrahydrofuran, 2-methyl tetrahydrofuran, 2, 5-dimethoxy tetrahydrofuran), dioxolane, dioxane, and independent or two or more sorts of mixed solvents of a dichloroethane can be used. They are a carbonate solvent, an ether solvent, and a furan solvent preferably [ among these ]. Although there will be especially no limit as an electrolyte salt in this invention if used as a usual electrolyte For example, LiBR<sub>4</sub> (R is a phenyl group and an alkyl group), LiPF<sub>6</sub>, LiSbF<sub>6</sub>, LiAsF<sub>6</sub>, LiBF<sub>4</sub>, LiClO<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>Li, (CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>NLi, 3(CF<sub>3</sub>SO<sub>2</sub>)CLi, C<sub>6</sub>F<sub>9</sub>SO<sub>3</sub>Li, and C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub> -- Li, LiAlCl<sub>4</sub>, etc. can be illustrated. It is the electrolyte of sulfonic-acid system anions, such as CF<sub>3</sub>SO<sub>3</sub>Li, 3(CF<sub>3</sub>SO<sub>2</sub>)NLi, 3(CF<sub>3</sub>SO<sub>2</sub>)CLi, C<sub>6</sub>F<sub>9</sub>SO<sub>3</sub>Li, and C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub>Li, preferably. Although the electrolytic solution is adjusted in the 0.5 mols/l. or more less than six mols [l. ] range, it is within the limits of 3.5 mols/l. from 0.8 mols/l. preferably. As a giant-molecule solid electrolyte, polyethylene oxide, polypropylene oxide, Polyvinylidene fluoride, polyacrylamide, etc. are made into a polymer matrix. The complex which dissolved the aforementioned electrolyte salt into the polymer matrix, or these gel bridge formation objects, The solid polymer electrolyte which graft-ized ionic dissociation radicals, such as low-molecular-weight polyethylene oxide and crown ether, to the polymer principal chain, Or the solid polymer electrolyte which contains ionic dissociation radicals, such as gel which added the solvent to these further, a low-molecular-weight polyethylene oxide chain, and crown ether, in a polymer frame, or the gel solid polymer electrolyte which made this contain said electrolytic solution is mentioned.

[0006] The lithium alloy which consists of a lithium metal, aluminum, silicon, copper, zinc or tin, and a lithium as a negative electrode in this invention, the carbon material which are occlusion and the host compound which can be emitted irreversibly about a lithium ion, and a ceramic ingredient can be

illustrated. The conductive carbon body or the insulating or half-conductive carbon body obtained as a carbon material by calcinating synthetic macromolecules, such as naturally-occurring polymers or phenol system resin, PAN system resin, furan system resin, polyamide system resin, and polyimide system resin, can be illustrated. It is desirable to use a graphite ingredient as a main constituent as a carbon body of this invention. As a graphite ingredient of this invention, the artificial graphite which used pitch coke besides a natural graphite, needle coke, a fluid coke, GIRUSONA corks, etc. as the raw material can be illustrated. As positive active material of the nonaqueous secondary lithium cell of this invention  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{CoO}_2$ ,  $\text{NiO}_2$  and  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{V}_3\text{O}_8$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{Fe}_2(\text{MoO}_4)_3$ , the metallic oxide of  $\text{Fe}_2(\text{WO}_4)_3$  grade, Metallic sulfide, such as  $\text{TiS}_2$ ,  $\text{MoS}_2$ , and  $\text{FeS}$ , these compounds and multiple oxides of a lithium, One sort or complex beyond it chosen from conductive polymers, such as polyacetylene, the poly aniline, polypyrrole, the poly thiophene, the poly alkyl thiophene, the poly carbazole, the poly azulene, and a poly diphenyl benzidine, and a carbon body can be illustrated. As an electrolyte, the electrolytic solution and the solid electrolyte which were mentioned above are used. Moreover, a separator can be used as occasion demands. The nonwoven fabric or textile fabrics which is low resistance, and the thing excellent in solution holdout is used, for example, is chosen from one or more sorts of quality of the materials, such as glass, polyester, Teflon, and polypropylene, to the ionic migration of an electrolytic solution as a separator is mentioned. Although especially the gestalt of the cell of this invention is not limited, it can mount in the cell of various gestalten, such as coin, a sheet, a cylinder, and gum. An example explains this invention still more concretely below.

[0007]

[Example]

The example 1 poly aniline 30 weight section was dissolved in the N-methyl-2-pyrrolidone of the 170 weight sections, and the vanadium pentoxide 70 weight section was further distributed by the sand mill. To both sides of 25-micrometer etched aluminum foil, spreading desiccation was carried out by the blade coating machine, and this coating solution was used as the positive electrode of 60 micrometers of one side. The negative-electrode active material layer was created so that the natural-graphite 80 weight section of 99.9% of purity and the tetrafluoroboric acid lithium 10 weight section might be distributed in the 10wt% N-methyl-2-pyrrolidone solution 100 weight section of polyvinyl pyridine system resin (extensive Sakae chemistry), it might consider as a negative-electrode coating solution and the thickness of one side might become 80 micrometers to both sides of an SUS foil (thickness of 20 micrometers) (drying temperature of 100 degrees C). Through the 25-micrometer separator [Celgard 3501 and a trade name (die cel company make)], the laminating of a positive electrode and the negative electrode was carried out, they were wound, and it considered as the cell of AA size. In the aforementioned (3) formula, to said solution, m added to the ethylene carbonate / dimethoxyethane (1:1) solvent which contained two mol / of  $2\text{NLi(s)}$  l. as the electrolytic solution ( $\text{CF}_3\text{SO}_2$ ) 3% of the weight, and used for it the silicone system compound which the both ends of 1, and r and k3 are n, and is a methyl group. The comparison performed the thing except a silicone system compound as an example 1 of a comparison. The cell property of the cell of this example and the example 1 of a comparison was shown in the following table 1.

[0008] It was presupposed that it is the same as that of an example 1 except having used the solid electrolyte solution shown below instead of the example 2 electrolytic solution. The photopolymerization nature solution which consists of the tetrafluoroboric acid lithium 20 weight section, the propylene carbonate 51 weight section, 1, the 2-dimethoxyethane 16 weight section, the polyoxyethylene acrylate 12.8 weight section, the trimethylol propane acrylate 0.2 weight section, and the benzoin-iso-propyl-ether 0.02 weight section was used as the solid polymer electrolyte solution. Tales-doses addition of the silicone system compound used for this solid electrolyte solution in the example 1 was carried out. This adjustment liquid is heated and solidified after pouring in like the electrolytic solution. The comparison performed the thing except a silicone system compound as an example 2 of a comparison. The cell property of this example and the example 2 of a comparison was shown in the following table 1.

[Table 1]

An example 1 An example 2 The example 1 of a comparison Example of comparison 2 energy 485mAh  
(s) 465mAh 388mAh 370mAh cycle property 500 times 500 times 350 times 400 times CmA [ 2]  
discharge 88% 81% 66% 58%CmA [ 1] 1-hour charge 86% 80% 74% 69% energy : The spark-  
discharge-energy cycle property after repeating charge and discharge 10 times by 1/2CmA: Count of a  
cycle until energy becomes 70% by the charge and discharge of 1/2CmA.  
2CmA discharge, 1CmA 1 hour charge: Incidence-rate 2CmA discharge:2CmA constant current 2.5V  
cut-off discharge 1CmA1 hour charge:1CmA constant current 3.7V low-battery charge 1 hour [0009] to  
the above-mentioned energy  
[Effect] According to this invention, the highly efficient nonaqueous lithium secondary battery which is  
excellent in a cycle property and can be charged also with high current density was offered.

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[Translation done.]